

WATER QUALITY SAMPLING IN THE  
DUWAMISH WATERWAY NEAR MONSANTO CHEMICALS COMPANY  
December 1983

Jane D. Gendron  
Donald R. Heinle

February 1984

CH2M HILL

## CONTENTS

	<u>Page</u>
Introduction	1
Summary	2
Collection Technique	3
Sample Compositing Technique	3
Sample Storage and Shipping Procedure	4
Analytical Procedure	6
Analytical Results	7
Nonpriority Pollutants	8
References	11
Appendix	

## TABLES

1	Volume of Water Collected Each Day for Composite Samples	5
2	Results of Priority Pollutant Metals Analysis	9
3	Nonpriority Pollutant ICP Analysis Results	10

INTRODUCTION

CH2M HILL was contracted by Monsanto to sample water from the Duwamish waterway in the vicinity of their Seattle plant and have this water analyzed for the 129 priority pollutants, and other water-quality parameters. This report presents the sampling techniques, analytical protocol, and results of the priority pollutant and non-priority pollutant analyses.

SUMMARY

The Duwamish waterway was sampled at five sampling points on three consecutive days in December 1983. Three sampling points were from surface water while two points were subsurface in the salt wedge. Water was composited and sent to analytical laboratories for analysis of the 129 priority pollutants (except asbestos). Analysis was also done of several nonpriority pollutant metals.

Negative results were obtained on all samples from analyses of volatiles, base/neutral compounds, acids, pesticides, PCB's, and cyanide. Ten priority pollutant metals were detected, primarily from the salt wedge sampling points, including relatively high levels of copper and zinc. Thallium and zinc were the only metals detected at greater amounts downstream than upstream in the surface waters.

COLLECTION TECHNIQUE

Water was collected and composited from the Duwamish River adjacent to the Monsanto Seattle plant on December 7, 8, and 9, 1983. Three transect locations were sampled each day during the last 2 hours of a falling tide. Transects U and D were based on the Monsanto Seattle Plant Environmental Assessment--Priority Pollutants Report dated February 19, 1979 (Figure 1). A Hydrolab Model 2000 was used to determine the presence of a salt wedge in the river. Because saline water was detected at approximately 4 meters at midtransect D (downstream from the plant), subsurface samples were taken at transects D and U (upstream from the plant). A total of five samples was obtained:

- o D1--surface sample, transect D
- o D2--subsurface sample (depth 7 meters), transect D
- o U1--surface sample, transect U
- o U2--subsurface sample (depth 4 meters), transect U
- o S1--surface sample, eastside boat slip

Transect D1 was composed of three sampling points: D1.1, D1.2, and D1.3 (Figure 1). Transect D2 was at the same location as sampling point D1.2 but was sampled at a depth of 7 meters. Transect U1 was composed of two sampling points, U1.1 and U1.2, with transect U2 being a subsurface (4 meters deep) single sampling point located midway between U1.1 and U1.2. Transect S1 was a surface transect composed of two sampling points at the mouth of Port of Seattle's boat slip on the east side of the river, along the southern boundary of the Monsanto plant. Because of the presence of large docked ships in this slip, S1.1 was located almost midpoint in the slip.

Samples were collected from an oar-powered 13-foot Avon inflatable raft in the following order: D1, D2, U1, U2, S1. Surface water was collected from the upstream side of the raft. Calibrated glass jars with aluminum-covered lids (cleaned by Amtest Laboratories) were submerged 6 to 10 inches below surface waters, opened, and then relidded and retrieved. Subsurface samples were collected using a Teflon-coated Niskin bottle. Detailed trip notes, including Hydrolab and conductivity/salinity analysis results, are contained in Appendix A.

SAMPLE COMPOSITING TECHNIQUE

Calibrated glass jars were used to measure water samples for compositing. Composite containers were cleaned and prepared

by the analytical laboratory doing analyses. Following is a list of collecting containers used in this study.

<u>Analysis</u>	<u>Container</u>	<u>Laboratory</u>
Priority Pollutants (nonvolatile)	1/2-gal. amber glass bottle	CH2M HILL Montgomery
Priority Pollutants (volatile)	Teflon-diaphrased glass vials	CH2M HILL Montgomery
Metals--ICP	120-ml plastic vial	Amtest Inc.
Metals-atomic adsorption	Quart plastic cuvettes	CH2M HILL Corvallis
Cyanide	Quart plastic cuvettes	CH2M HILL Corvallis

Table 1 lists volumes of water collected each day from each transect and sampling point that comprised the total composite sample. Water collected in vials for volatile priority pollutant analysis was composited in the laboratory just prior to analysis.

#### SAMPLE STORAGE AND SHIPPING PROCEDURE

Samples were maintained in chain-of-custody control during this project. They were stored in ice chests and placed in a locked facility each night prior to shipping. Samples to be analyzed by CH2M HILL laboratories were shipped by Air Express, and samples to be analyzed by Amtest were hand delivered following the completion of sampling.

Table 1  
VOLUME OF WATER COLLECTED EACH DAY  
FOR COMPOSITE SAMPLES  
(ml unless otherwise noted)

Analysis	Laboratory	Transect D1			Transect D2	Transect U1		Transect U2	Transect S1		Transect Total
		D1.1	D1.2	D1.3	D2	U1.1	U1.2	U2	S1.1	S1.2	Volume
Priority Pollutants	CH2M HILL (MGM)	150	300	150	600	300	300	600	300	300	2 liters
Volatiles	CH2M HILL (MGM)	2 vials	2 vials	2 vials	2 vials	2 vials	2 vials	2 vials	2 vials	2 vials	varied
Metals	CH2M HILL (CVO)	150	300	150	600	300	300	600	300	300	2 liters
CN	CH2M HILL (CVO)	75	150	75	300	150	150	300	150	150	1 liter
ICP Metals	Amtest	10	20	10	40	20	20	40	20	20	120 ml

#### ANALYTICAL PROCEDURES

All tests were performed in accordance with current Environmental Protection Agency guidelines. Priority pollutants including volatiles, base/neutral compounds, acids, pesticides, and PCB's were analyzed using the following methodologies by the CH2M HILL Montgomery laboratory:

Priority pollutants--The samples were analyzed in accordance with procedures described in Methods 608, 624, and 625, EPA-600/4-82-057 (1982).

Analytical instrumentations used in these analyses were the Finnigan Model 4021 Gas Chromatograph/Mass Spectrometer/Data System equipped with a Tekmar LSC-1 Liquid Sample concentrator and the Varian Model 3700 Gas Chromatograph equipped with flame ionization, electron capture, and thermionic specific detectors. Parameters analyzed for and corresponding method detection limits for these analyses are contained in Appendix Tables B-1 through B-4.

Methodology used by the CH2M HILL Corvallis laboratory for metals and cyanide analyses was as documented in the EPA reference Methods for Chemical Analysis of Water and Waste, No. 600/4-79-020, March 1979. Specific methods for the various elements and compounds were: Sb, 204.2; As, 206.2; Be, 210.1; Cd, 213.2; Cr, 218.2; Cu, 220.1; Pb, 239.2; Hg, 245.1; Ni, 249.1; Se, 270.2; Ag, 272.2; Tl, 279.1; Zn, 289.1; and CN, 335.2.

Parameters analyzed for and method detection limits for these analyses are contained in Appendix Table B-5.

The multi-element Inductively Coupled Plasma Analysis (ICP) conducted by the Amtest Inc. Seattle laboratory was conducted according to EPA Test Method 200.7 from EPA reference Methods for Chemical Analysis for Water and Waste, No. 600/4-79-020 dated March 1979. Parameters analyzed for and method detection limits for this analysis are listed in Appendix Table B-6.



## ANALYTICAL RESULTS

Priority Pollutants. Samples were analyzed for all 129 priority pollutants with the exception of asbestos. Results from volatiles, base/neutral compounds, acids, pesticides, and PCB's were all below method detection limits. The 13 priority pollutant metals were analyzed by flame, furnace, or cold vapor atomic adsorption (AA), and 10 of these metals were also analyzed by ICP method (Appendix Table B-6). Table 2 lists results from these metal analyses. Only those parameters found above the detection limit are listed. Cyanide levels in all samples were below detection limits.

Of interest in these metal results are the copper and zinc levels reported for salt wedge samples D2 and U2. Flame AA tests results for copper were 160 µg/L for both samples while the ICP test method results were 190 µg/L. These values are high compared to several Duwamish study results. U.S. Army Corps of Engineers (1982) reported maximum copper levels in the Duwamish at river mile 3.81 to be 46 µg/L. The salinity of the sample resulting in this maximum concentration is not included in the report. EPA data from its Duwamish River Survey Case No. 254J did not show any detection copper levels in the vicinity of Monsanto. Analytical methodology used in the AA analysis may not have adequately screened for the copper-enhancing aspects of the salt matrix in these samples; therefore, the results from flame AA analysis stated above could be as much as twice as high as they should be. However, because the ICP method resulted in similar copper levels and this analysis is fundamentally the same for fresh and salt water, test results may be accurate. Harper-Owes' 1983 report to Seattle Metro lists an annual Duwamish River salt wedge maximum copper level at approximately 100.

Zinc levels measured by flame AA in the salt wedge samples ranged from 84 µg/L upstream to 72 µg/L downstream. These values are twice as high as STORET data reported by U.S. Army Corps of Engineers (1982), which showed the maximum zinc level in the Duwamish River at river mile 3.81 to be 39 µg/L (salinity of the sample not being listed). Surface sample results from this survey were comparable to the zinc levels in the 1979 Monsanto report as well as storet data reported by U.S. Army Corps of Engineers (1982). Zinc, like copper, is subject to salt matrix interference in analysis of seawater. Measured levels are enhanced in seawater.

All surface water levels had reported metal levels below EPA criteria for protection of freshwater species with the exception of mercury in the east boat slip. The reported level was 0.6 µg/L, which is 0.1 µg/l above the detection limit.

NONPRIORITY POLLUTANTS

Thirteen nonpriority pollutant metals were also analyzed by the Inductively Coupled Plasma Emission (ICP) method. Table 3 lists the results of this analysis. Appendix Table B-6 includes the detection limits for these parameters.

Table 2  
RESULTS OF PRIORITY POLLUTANT METALS ANALYSIS  
( $\mu\text{g/L}$ )

<u>Metal</u>	<u>Downstream Surface</u>	<u>Downstream Salt Wedge</u>	<u>Upstream Surface</u>	<u>Upstream Salt Wedge</u>	<u>East Side Slip Surface</u>
<u>Atomic Adsorption Method</u>					
Antimony	<5	37	<5	15	<5
Arsenic	<5	23	<5	<5	<5
Cadmium	<0.5	1.3	0.5	<0.5	<0.5
Chromium (total)	<5	7	10	5	<5
Copper	<20	160	<20	160	<20
Mercury	<0.5	<0.5	<0.5	<0.5	0.6
Selenium	<5	25	<5	5	<5
Silver	1	5	1	3	1
Thallium	100	300	<100	100	<100
Zinc	29	72	17	84	16
<u>ICP Method</u>					
Copper	<15	190	<15	190	<15
Zinc	23	390	<15	37	<15

Note: Only those detected are listed.

Table 3  
NONPRIORITY POLLUTANT ICP ANALYSIS RESULTS  
( $\mu\text{g/L}$ )

Parameter	Station				
	Downstream Surface	Downstream Salt Wedge	Upstream Surface	Upstream Salt Wedge	Eastside Slip Surface
Aluminum	240	<150	200	570	180
Barium	5	53	4	18	4
Boron	600	3,070	480	1,770	550
Calcium	47,400	262,000	39,300	153,000	47,100
Iron	670	300	540	1,000	480
Magnesium	120,000	880,000	97,300	475,000	120,000
Manganese	48	30	41	50	42
Phosphorus	800	1,600	720	1,530	760
Potassium	37,100	263,000	30,200	150,000	37,500
Silicon	18,900	5,550	15,800	11,600	14,400
Sodium	1,100,000	7,600,000	790,000	4,100,000	968,000
Strontium	770	5,100	610	2,950	760
Titanium	<6	<6	<6	15	<6

Note: Only those detected are listed.

REFERENCES

U.S. Army Corps of Engineers. Draft Feasibility Report and Draft Environmental Impact Statement: East, West and Duwamish Waterways Navigation Improvement Study. 1982.

Hoogheem, Thomas J. Seattle Plant Environmental Assessment-- Priority Pollutants. Monsanto Company Report MDA-028. 1979.

Harper-Owes. Water Quality Assessment of the Duwamish Estuary. Prepared for Municipality of Metropolitan Seattle. 1983. 194 p plus Appendices.

APPENDIX

TRIP NOTES

December 7, 1983. Weather: overcast, cold, rain began at 14:00. Low slack tide at 13:10.

Launched raft from marina dock across from Monsanto Plant. Rowed to transect D and did Hydrolab profile at 12:40. Noted increase in temperature and conductivity at 4 meters (Table A-1). Hydrolab then became disfunctional. Returned to marina dock to obtain transect D sampling bottles. Collected samples in the following order: D1.1, D1.2, D1.3, and D2. An oily sheen was observed on surface of water collected at D2. Some water from D2 saved to run conductivity/salinity in lab. Returned to dock to obtain remaining sample bottles. Collected water from transect U at 14:00 in following order: U1.1, U1.2, and U2. Saved some water from U2 for conductivity/salinity analysis. Sampled transect S at 14:30 in order of S1.1 and S1.2. A ship was docked on south side of slip crossing transect S. Because of this, S1.1 was taken at approximately midpoint at the mouth of slip, downstream from the ship. Rust was evident on sides of ship and water was running off side of ship during sampling.

December 8, 1983. Weather: cold, windy, light drizzle. Low slack tide at 14:03.

Sampling order was same as previous day and water was saved from each transect, except U1, for conductivity/salinity analysis (Table A-1). Sampling occurred from 13:15 to 14:15. Same rusty ship in boat slip but no apparent runoff occurring. Smaller ship docked in front of rusty ship was pumping out water.

December 9, 1983. Weather: rain, cold, light wind. Low slack tide at 15:00.

Sampling order same as on previous days and was conducted from 14:00 to 15:00. Same ship noted on December 8 was still pumping water out and a heavy oil slick was observed in slip. When sampling was completed, samples were prepared for shipping to CH2M HILL in Montgomery and Corvallis and were mailed Air Express. Samples being analyzed by Amtest were hand-delivered to their Seattle laboratory at 16:30.

Table A-1  
WATER QUALITY RESULTS, DUWAMISH RIVER AT MONSANTO

<u>Date</u>	<u>Station</u>	<u>Depth (meters)</u>	<u>Temp. (°C)</u>	<u>Conductivity (micromhos)</u>	<u>Salinity (0/∞)</u>	<u>pH</u>
12/7	D1 (a)	surface	5.7	6,500	2.8 0/∞	6.94
		1	5.8	7,000	3.8 0/∞	6.67
		2	5.8	7,500	4.2 0/∞	6.47
		4	9.3	38,700	24.7 0/∞	6.06
	D2 (b)	7			30 0/∞	
	U2 (b)	4			16 0/∞	
12/8	D1 (b)	surface			4 0/∞	
	D2 (b)	7			22 0/∞	
	U2 (b)	4			8 0/∞	
	S1 (b)	surface			4 0/∞	

<sup>a</sup> Measured with a Hydrolab Model 2000 in field

<sup>b</sup> Measured with a YSI conductivity meter in Seattle CH2M HILL laboratory.



Table B-1  
 BASE/NEUTRAL COMPOUNDS ANALYZED FOR AND  
 METHOD DETECTION LIMIT  
 (Parts Per Billion or PPB Equivalent to µg/L)

Compounds	Method Detection Limit (PPB)	Compounds	Method Detection Limit (PPB)
Bis (2-chloroethyl) ether	10	4-Bromophenyl phenyl ether	10
1,3-Dichlorobenzene	10	Hexachlorobenzene	10
1,4-Dichlorobenzene	10	Phenanthrene	10
1,2-Dichlorobenzene	10	Anthracene	10
Bis (2-Chloroisopropyl) ether	10	Dibutyl phthalate	10
Hexachloroethane	10	Fluoranthene	10
N-nitroso-di-n-propylamine	10	Pyrene	10
Nitrobenzene	10	Benzidine	40
Isophorone	10	Butyl benzyl phthalate	10
Bis (2-Chloroethoxy) methane	10	2,3,7,8-Tetrachlorodibenzo-p-dioxin	10
1,2,4-Trichlorobenzene	10	Benzo (a) anthracene	10
Naphthalene	10	Chrysene	10
Hexachlorobutadiene	10	3,3'-Dichlorobenzidine	40
Hexachlorocyclopentadiene	10	Bis (2-ethylhexyl) phthalate	10
2-Chloronaphthalene	10	Di-n-octyl phthalate	10
Acenaphthylene	10	Benzo (b) fluoranthene	10
Dimethylphthalate	10	Benzo (k) fluoranthene	10
2,6-Dinitrotoluene	10	Benzo (a) pyrene	10
Acenaphthene	10	Indeno (1,2,3-cd) pyrene	10
2,4-Dinitrotoluene	10	Dibenzo (a,h) anthracene	10
Fluorene	10	Benzo (g,h,i) perylene	10
4-Chlorophenyl phenyl ether	10	N-nitrosodimethylamine	ND
Diethyl phthalate	10	Bis (chloromethyl) ether	ND
N-nitrosodiphenylamine	10		
1,2-Diphenylhydrazine	10		

ND = Not determined.

Table B-2  
ACID COMPOUNDS ANALYZED FOR AND METHOD DETECTION LIMIT  
(Parts Per Billion or PPB Equivalent to  $\mu\text{g/L}$ )

<u>Compounds</u>	<u>Method Detection Limit (PPB)</u>
Phenol	10
2-Chlorophenol	10
2-Nitrophenol	10
2-4-Dimethylphenol	10
2-4-Dichlorophenol	10
4-Chloro-3-methylphenol	10
2,4,6-Trichlorophenol	10
2,4-Dinitrophenol	50
4-Nitrophenol	10
2-Methyl-4,6-dinitrophenol	50
Pentachlorophenol	10

Table B-3  
VOLATILE COMPOUNDS ANALYZED FOR AND  
METHOD DETECTION LIMIT  
(Parts Per Billion or PPB Equivalent to  $\mu\text{g/L}$ )

Compounds	Method Detection Limit (PPB)
Chloromethane	10
Bromomethane	10
Vinyl Chloride	10
Chloroethane	10
Methylene Chloride	5
Trichlorofluoromethane	5
1,1-Dichloroethene	5
1,1-Dichloroethane	5
Trans-1,2-Dichloroethene	5
Chloroform	5
1,2-Dichloroethane	5
1,1,1-Trichloroethane	5
Carbon Tetrachloride	5
Bromodichloromethane	5
1,2-Dichloropropane	5
Trans-1,3-Dichloropropene	5
Trichloroethylene	5
Benzene	5
Dibromochloromethane	5
1,1,2-Trichloroethane	5
Cis-1,3-Dichloropropene	5
2-Chloroethyl vinyl ether	10
Bromoform	5
1,1,2,2-Tetrachloroethane	5
Tetachloroethylene	5
Toluene	5
Chlorobenzene	5
Ethyl Benzene	5
Acrylonitrile	100
Acrolein	100
Dichlorodifluoromethane	ND <sup>1</sup>

<sup>1</sup>ND = Not Determined

Table B-4  
PESTICIDES/PCB's ANALYZED FOR AND METHOD  
DETECTION LIMIT  
(Parts Per Billion or PPB Equivalent to  $\mu\text{g/L}$ )

Compounds	Method Detection Limit (PPB)
Aldrin	0.2
a-BHC	0.2
b-BHC	0.2
d-BHC	0.2
g-BHC	0.2
Chlordane	0.5
4,4'-DDD	0.2
4,4'-DDE	0.2
4,4'-DDT	0.2
Dieldrin	0.2
Endosulfan I	0.2
Endosulfan II	0.2
Endosulfan Sulfate	0.5
Endrin	0.2
Endrin Aldehyde	0.5
Heptachlor	0.2
Heptachlor Epoxide	0.2
Toxaphene	3.0
PCB-1016	2.0
PCB-1221	2.0
PCB-1232	2.0
PCB-1242	2.0
PCB-1248	2.0
PCB-1254	2.0
PCB-1260	2.0

Table B-5  
METALS ANALYZED BY ATOMIC ADSORPTION  
METHODOLOGY AND DETECTION LIMIT

<u>Metal</u>	<u>Detection Limit (<math>\mu\text{g/L}</math>)</u>	<u>AA Method Used<sup>1</sup></u>
Antimony	5	A
Arsenic	5	A
Beryllium	10	B
Cadmium	0.5	A
Chromium (total)	5	A
Copper	20	B
Cyanide	5	-
Lead	5	A
Mercury	0.5	C
Nickel	50	B
Selenium	5	A
Silver	1	A
Thallium	100	B
Zinc	5	B

<sup>1</sup>  
A = Graphite Furnace AA  
B = Direct Flame AA  
C = Cold Vapor AA

Table B-6  
PARAMETERS ANALYZED FOR BY ICAP METHODOLOGY  
AND DETECTION LIMITS

Parameter		Detection Limit ( $\mu\text{g/L}$ )
Aluminum	Al	150
Antimony <sup>a</sup>	Sb	150
Arsenic <sup>a</sup>	As	300
Barium	Ba	1
Beryllium <sup>a</sup>	Be	3
Bismuth	Bi	500
Boron	B	10
Cadmium <sup>a</sup>	Cd	25
Calcium	Ca	10
Chromium <sup>a</sup>	Cr	30
Cobalt	Co	20
Copper <sup>a</sup>	Cu	15
Iron	Fe	30
Lead <sup>a</sup>	Pb	80
Magnesium	Mg	1
Manganese	Mn	3
Molybdenum	Mo	40
Nickel <sup>a</sup>	Ni	25
Phosphorus	PO <sub>4</sub>	400
Potassium	K	10
Silicon	SiO <sub>2</sub>	80
Silver	Ag	30
Sodium	Na	100
Strontium	Sr	1
Tin	Sn	30
Titanium	Ti	6
Vanadium	V	10
Zinc <sup>a</sup>	Zn	15

<sup>a</sup>Priority pollutant

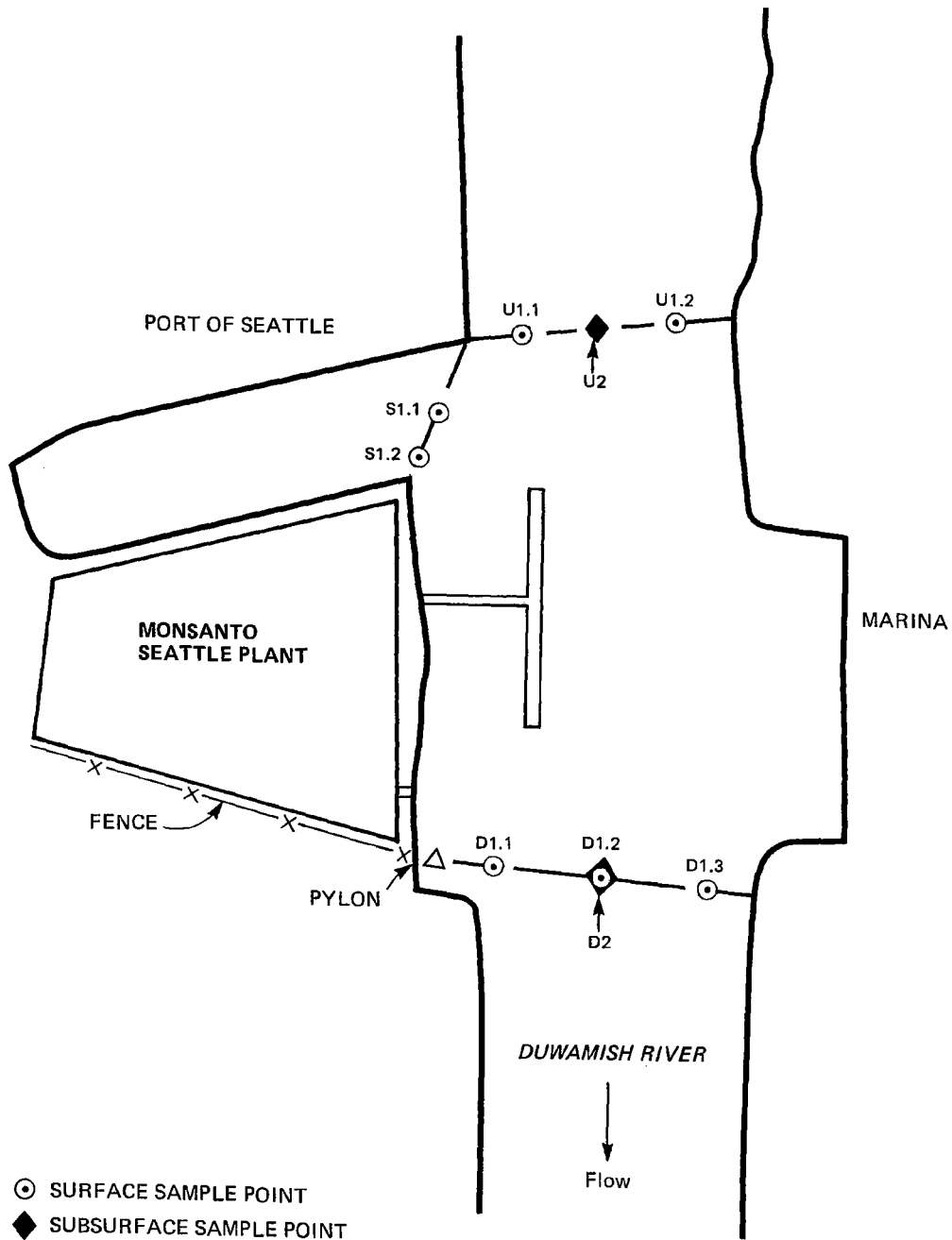


Figure 1  
DUWAMISH RIVER  
FIELD SAMPLING POINTS  
DECEMBER 1983